PRODUCTION OF HYDROGEN FROM LOW HEATING VALUE FUEL GASES BY THE BEACON PROCESS

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Background

BEACON is an acronym for Btu Extraction And CONcentration. The process is based on the catalytic deposition of a highly reactive carbon (C*) from low heating value gases (LBG = low Btu gas). As illustrated in Figure 1 the BEACON process involves circulating a very easily fluidizable, solid carbonaceous material containing a catalyst between two fluid bed reactors.

In one reactor the solid material contacts the low heating value fuel gas feedstock resulting in the rapid deposition of very reactive carbonaceous material by reactions of the type:

$$2CO \longrightarrow C^* + CO_2 \quad (1)$$

$$CO + H_2 \longrightarrow C^* + H_2O \quad (2)$$

$$CH_n \longrightarrow C^* + n/2\ H_2 \quad (3)$$

Thus, in this reactor the incoming carbonaceous material and catalyst are enriched in carbon content through the deposition process and the low heating value fuel gas is depleted in energy content by an amount which is nearly equal to the heating value of the deposited carbon. The fuel gas is brought into the fluid bed carbon deposition reactor at near ambient temperature and the depleted fuel gas exits the reactor at 450°C to 550°C. Thus, most of the exothermic heat associated with carbon deposition is taken up in the depleted fuel gas as sensible heat in the nitrogen diluent, available for steam or power generation.

The carbon rich, solid, carbonaceous material and associated catalyst produced in the deposition reactor is separated from depleted fuel gas and circulated to a second reactor where the material is contacted with steam. In this reactor the steam-carbon reaction is very rapid at temperatures as low as 550°C or some 300°C below the temperature at which coals or chars will react effectively with steam. Depending on operating conditions (pressure, temperature and steam utilization) and catalyst type, either of the following overall reactions may predominate:

$$2C^* + 2H_2O \longrightarrow CH_4 + CO_2 \text{ (Methane Option)} \quad (4)$$

or

$$C^* + 2H_2O \longrightarrow 2H_2 + CO_2 \text{ (Hydrogen Option)} \quad (5)$$

Heat must be supplied for the steam-carbon reactions described above. However, since the reaction temperature is modest (550-650°C) this heat can readily be supplied (indirectly) from the hot, depleted, and fully combusted fuel gas. Thus, a part of the residual energy content of the depleted fuel gas is used to drive the

steam-carbon reactions. This endothermic heat of reaction, of course, adds to the final total heating value of product methane or hydrogen at near 100% efficiency. That is to say, the higher heating value of the product methane or hydrogen rich gas exceeds the heating value of the reactant carbon by an amount equal to the endothermic heat of reaction.

To complete the solids circulation loop, carbon lean solids from the steaming reactor are returned to the carbon deposition reactor for carbon enrichment. For example, the carbon lean solids may contain 50-60% carbon and the carbon rich solids may contain 80-90% carbon.

In the BEACON technology there are three key areas of technical advantage:

1. A novel chemistry which results in very fast reactions at moderate temperature.

2. An ability through modifications of operating conditions and catalysts to produce either methane or hydrogen as a primary product.

3. An intermediate carbonaceous material and associated catalyst which has excellent fluid mechanical properties.

In both the carbon deposition and steaming reactions, utilizing the catalysts developed, near equilibrium compositions are obtained with gas-solid contact times that are well within commercially practical ranges. Carbon deposition is rapid above 400°C and the steam-carbon reaction becomes effective above 550°C.

The fluid mechanical properties of unsupported carbonaceous material are very different from other solid powders. Of great importance is the fact that this material fluidizes very well at commercially reasonable gas velocities.

Experimental Approach and Theoretical Comparisons

The objective of the work described in this paper was to demonstrate the viability of a catalyst system which is selective for hydrogen production in the reaction of deposited carbon with steam. In this case we want to suppress the formation of methane as completely as possible in the steaming reaction. In assessing our results we will compare the experimental measurements with two types of equilibrium calculations. The first type of thermochemical calculation allows methane and all other possible species to be present in the equilibrium product mixture. The second calculation excludes all hydrocarbon species (principally CH_4) from the calculation and gives a pseudo-equilibrium distribution of product species under conditions where methane is not allowed to form.

The experimental system shown in Figure 2 and described previously (Ref. 1) was used in the investigation. The system is a two reactor apparatus based on a variable differential pressure transfer line concept for the transfer of solids between BEACON carbon deposition and carbon gasification reactors. The "huff-puff" transfer system does not require gas/solids separation prior to transfer, and therefore it is simpler than a lock-hopper type system for fluidized bed operations. Adaptation of the "huff-puff" concept in BEACON processing was considered possible because of the unique properties of the solids-gas mixtures which give rise to stable fluid beds.

In this tandem concept the two reactors are connected with a fluid bed transfer line located below the top of the beds. Transfer is accomplished by establishing a small differential pressure between the two reactors and opening the transfer line valve. Solids are transferred back and forth by changing the sign of the differential pressure. About 10% of the bed is transferred each time. The

two reactors can be operated at different operating conditions, except pressure, as needed to optimize deposition or gasification; pressure, however, must be nearly equal in the reactors. Two additional requirements are that the relative size of the two reactors be such that the quantities of carbon deposited and gasified per unit time are equal and that both reactors operate under fluidized bed conditions. Ranges of allowable operating conditions were as follows:

Parameter	Deposition Reactor	Steaming Reactor
Temperature	400-600°C	500-750°C
Pressure	1-10 Atm	1-10 Atm
Gas Velocity	5-45 cm/sec	5-56 cm/sec
Feed Gas Composition:		
o Nitrogen	10-85%	0-50%
o Hydrogen	5-30%	0
o Carbon Monoxide	10-50%	0
o Carbon Dioxide	0-10%	0
o Steam	0	50-100%

The system shown in Figure 2 consists of the following sections: gas feed system, steam boiler, carbon deposition reactor, steam gasification reactor, product gas cleanup train, reactor pressure control and product gas metering system, solids transfer system, and data acquisition system. The deposition reactor has a 6-inch inside diameter and the gasifier a 3-inch inside diameter (the difference in reactor size was dictated by the difference in deposition and gasification rates at the desired operating ranges). Both reactors are constructed from 316 stainless steel parts and are surface aluminized by the Alon Process to prevent catalyst contamination from the reactor walls (especially through carburization of the deposition reactor walls).

Carbon deposition and steaming took place simultaneously and at equal rates. Typical rates were approximately 400 grams carbon deposited or steamed per hour; thus, the net solids transfer from the deposition reactor to the gasifier was about 400 grams per hour. Nominally, transfers were conducted about once an hour; approximately 700 grams were transferred from the carburizer to the gasifier and about 300 grams in the opposite direction. These quantities represented about 10% of the total solids in the system so that the disturbance of steady state was minor (the transfer was noticeable for one gas chromatogram of the product gas of the gasifier but had no effect on the product gas of the carburizer). Solids were transferred from the bottom of the reaction zone of one reactor to the top of the reaction zone of the other reactor; occasionally, the direction was reversed. The two-directional transfer operation took about three minutes, including the time (about one minute) required for system equilibration between the single transfers.

A single batch of catalyst solids (No. 11) which had shown outstanding activity and selectivity (methane suppression) in previous, small atmospheric pressure laboratory tests was subjected to approximately 375 hours of processing (simultaneous carbon deposition and steaming in separate reactors). Processing time consisted of 265 hours of steady state operation and about 110 hours of transient operation (mostly start-up and shutdown). Steady state processing time consisted of about 200 hours of operation at 4.4 atmospheres (50 psig), 50 hours at 6.1 atmospheres (75 psig), and 15 hours at 7.8 atmospheres (100 psig) reactor pressure.

The nominal conditions during the multi-cycle testing of Catalyst No. 11 solids were 620°C and six centimeters per second linear superficial velocity for steam gasification and 400°C and 15 centimeters per second velocity for carbon deposition at the above three pressures. The feed to the gasifier was 100% steam, but in the reaction zone it was diluted by approximately 20% v/v nitrogen gas used to maintain the DP legs and solids transfer lines free of solids (purge gas). The nominal deposition reactor feed gas composition was 10% v/v CO, 5% v/v H_2, with the balance being nitrogen gas.

Results

Figure 3 summarizes the catalyst performance data generated during the 375 hours of simultaneous operation (265 hours of steady state processing). The top portion of Figure 3 summarizes the performance of the carbon deposition operation expressed in terms of "fuel" (CO and H_2) utilization. Carbon monoxide utilization was near equilibrium and constant. Hydrogen utilization was high and also constant throughout the 265 hours of steady state processing. The middle and bottom graph of Figure 3 summarize the data pertaining to the performnance of the steam gasification operation. Over the range of pressures investigated, nominally 80% methane suppression was obtained at equilibrium steam utilization for the duration of the 265 hours of steady state operation. Neither the deposition nor the gasification data revealed any trend of catalyst deterioration.

The stability of Catalyst No. 11 performance is also evident from the data presented in Tables 1 and 2, where a set of product gas composition data (dry and nitrogen free) is presented for every 50 hours of steady state operation. Table 1 summarizes steaming data which are compared to compositions predicted by thermodynamics for equilibrium operation at 650°C, 4.4 and 6.1 atmospheres (50 and 75 psig). The comparison of experimental data to equilibrium composition reveals that after 50 hours of processing time some CO (and steam) have shifted to CO_2 and H_2. It is expected that this shift occurs in the transition and expansion zone of the reactor. This conclusion is consistent with on-line DP monitoring which indicated an increase in themass of solids contained in the expansion zone during the latter part of testing. Table 2 presents data for the carbon deposition operation. Product gas composition stability is excellent, CO conversion is high and approaches equilibrium values, but hydrogen conversion is significantly lower than equilibrium predicted values.

Including laboratory data, four pressures were investigated during the course of performance testing of Catalyst No. 11. Figure 4 illustrates the effect of reactor pressure on steam utilization and methane concentration in the product gas during steam gasification of Catalyst No. 11 solids at 620°C. The experimental data are compared to thermodynamically predicted values for the same conditions (solid lines on Figure 4). Methane suppression was nominally 80% or greater at all pressures investigated. The experimental values of the steam utilization fall in between the thermodynamically predicted values represented by the solid lines for normal and zero methane equilibria. This was expected since methane suppression was not complete.

Acknowledgment

This work was performed by TRW under Deparment of Energy Cooperative Agreement DE-FC21-80MC14400.

Reference

1. Blumenthal, J. L., et al, "Tandem Reactor Testing of the BEACON System," 11th Energy Technology Conference, March 20, 1984, Washington, D.C.

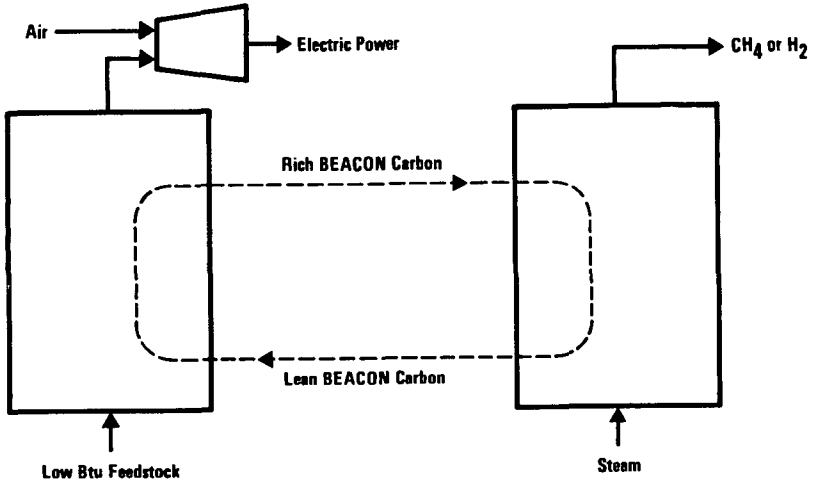
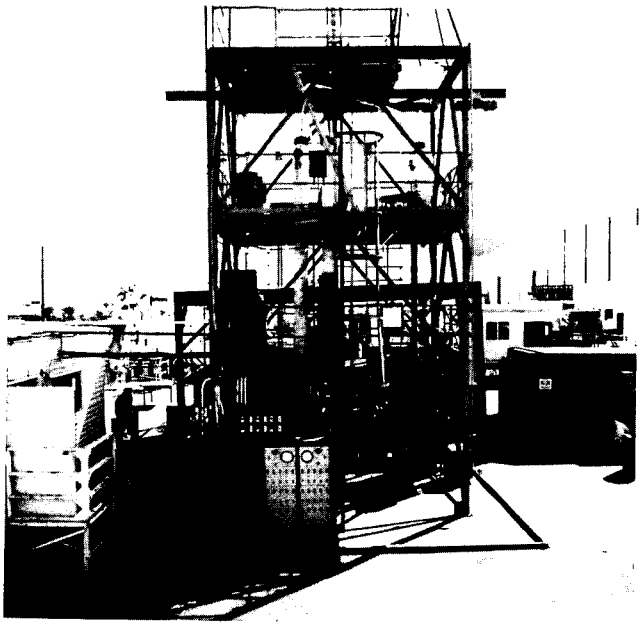


FIGURE 1. BEACON PROCESS CONFIGURATION



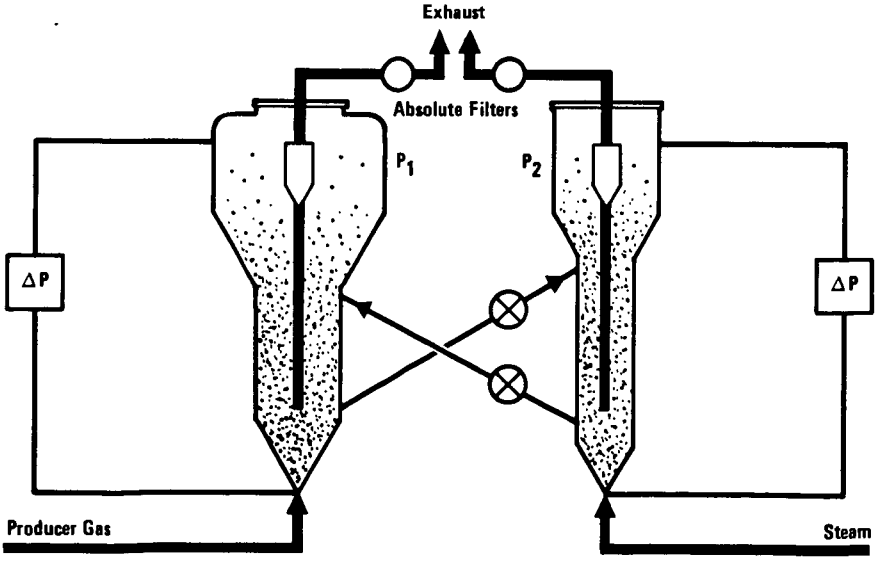
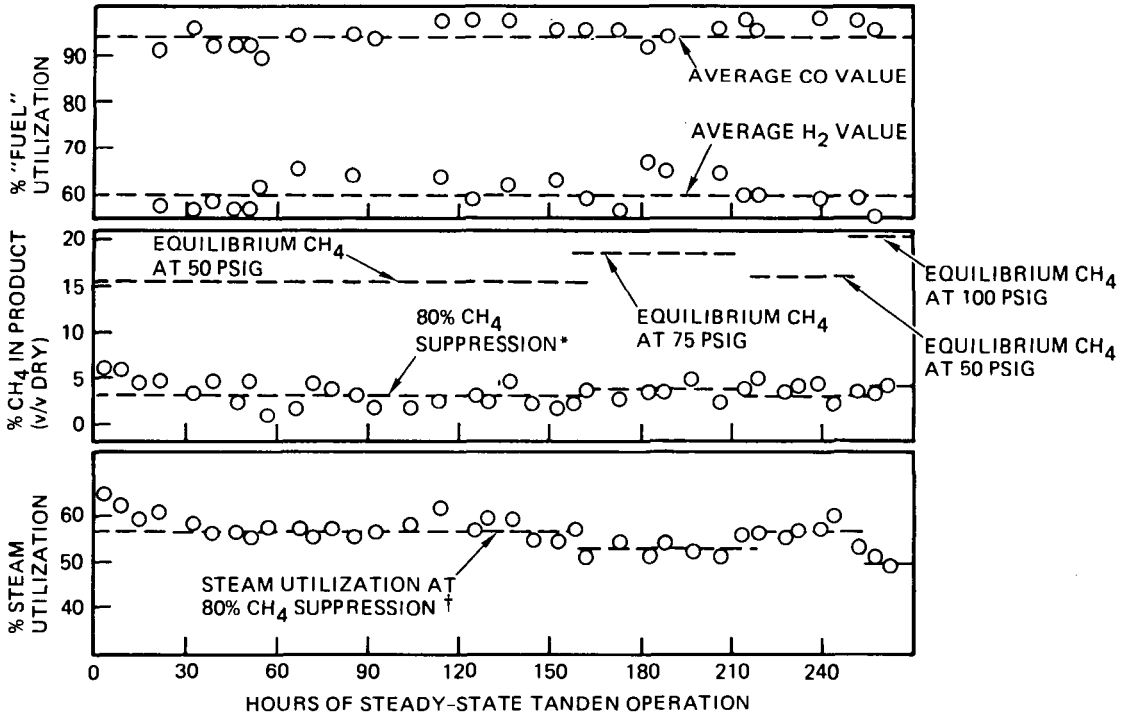


FIGURE 2. EXPERIMENTAL APPARATUS



*EQUILIBRIUM CH_4 AT 50/75/100 PSIG IS 15.8/18.3/20.2 PERCENT. AT 80% SUPPRESSION, METHANE IS 3.2/3.7/4.0 PERCENT RESPECTIVELY.

†EQUILIBRIUM STEAM UTILIZATION AT :50/75/100 PSIG IS 64.7/63.0/61.8 PERCENT AT NORMAL METHANE (METHANE IS ALLOWED TO FORM) AND 54.2/50.5/47.7 PERCENT AT 100% CH_4 SUPPRESSION (METHANE IS NOT PERMITTED TO FORM). BY INTERPOLATION, AT 80% CH_4 SUPPRESSION, STEAM UTILIZATION SHOULD BE 56.3/33.0/50.5 PERCENT, RESPECTIVELY.

FIGURE 3. STABILITY TESTING OF CATALYST NO. 11 IN TANDEM REACTORS (400°C/620°C, 50/75/100 PSIG)

TABLE 1. STABILITY OF PRODUCT GAS COMPOSITION IN TANDEM REACTORS (STEAM GASIFICATION OF CATALYST NO. 11 SOLIDS AT 620°C, 50 PSIG AND 75 PSIG)

	Thermodynamically Predicted Composition				Product Composition, 5 v/v Versus Hours of Operation				
	50 Psig		75 Psig						
Specie	Normal	Zero Methane	Normal	Zero Methane	50 Hrs*	100 Hrs*	150 Hrs*	200 Hrs**	250 Hrs*
CH_4	15.8	0	18.3	0	4	3	2	3	2
H_2	41.2	62.5	38.4	62.9	57	61	60	63	62
CO	13.0	12.3	11.5	11.0	12	9	7	6	7
CO_2	30.0	25.2	31.8	26.1	27	27	31	28	29
% Steam Utilization	64.7	54.2	63.0	50.5	55	60	54	54	58
% Methane Suppression	0	100	0	100	75	81	87	84	87

- Typical Feed Composition: 80% v/v Steam, 20% v/v N_2 (Nitrogen was used to purge DP probes)

* 50 psig data

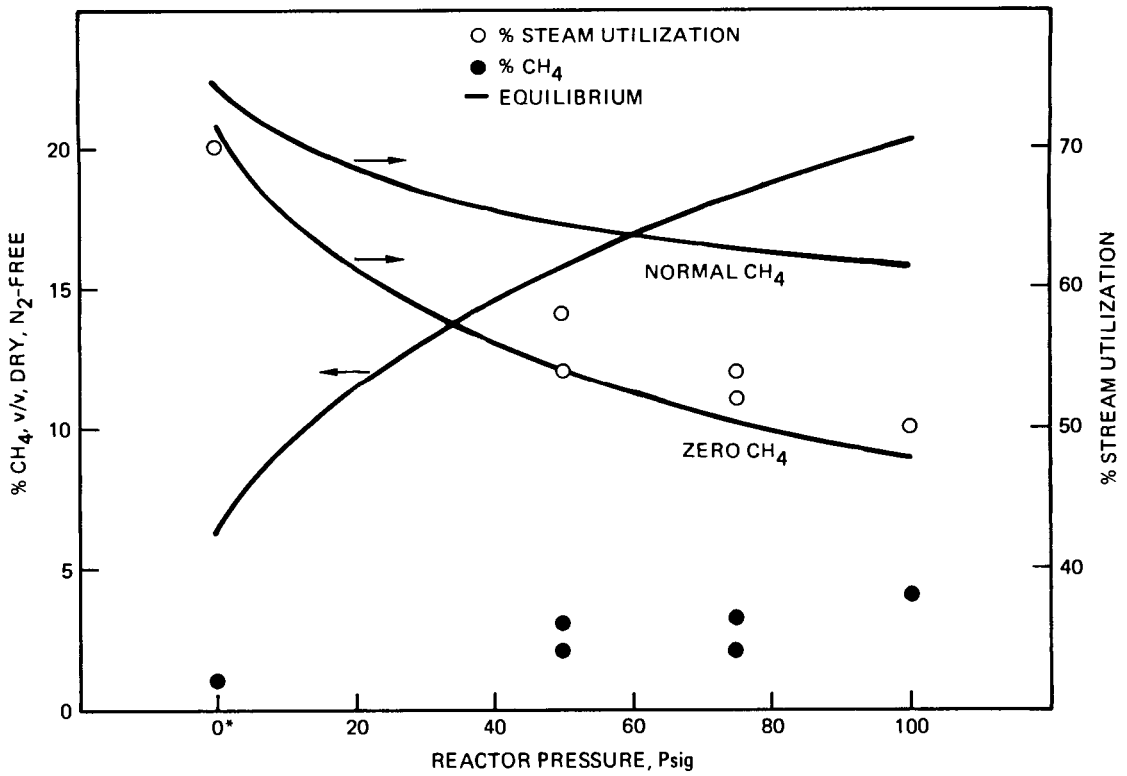
** 75 psig data

TABLE 2. STABILITY OF PRODUCT GAS COMPOSITION IN TANDEM REACTORS (CARBON DEPOSITION ON CATALYST NO. 11 SOLIDS AT 400°C, 50 PSIG AND 75 PSIG)

Specie	Thermodynamically Predicted Composition 50 Psig	50 Psig	75 Psig	Hours of Operation (Test Data) 50 Hrs*	100 Hrs*	150 Hrs*	200 Hrs**	250 Hrs*
A. Feed Gas Composition, % v/v (Balance Nitrogen)								
CO	9	13	13	9	13	11	13	11
H_2	4	6	6	4	6	5	6	4
B. Product Gas Composition, % v/v (Nitrogen Free)								
CH_4	8.5	10.0	10.6	2	4	4	6	4
H_2	16.1	14.5	12.9	28	25	26	29	25
CO	1.6	1.4	1.2	12	4	6	4	5
CO_2	73.8	74.1	75.3	58	67	64	61	66
C. Fuel Utilization								
% CO	99.2	99.4	99.5	92	97	96	97	97
% H_2	82.6	85.3	87.3	56	63	61	59	58

* 50 psig data

** 75 psig data



*AMBIENT PRESSURE DATA GENERATED AT 100% STEAM FEED. EQUILIBRIUM CURVES AND PRESSURIZED DATA ARE FOR A 80% v/v STEAM, 20% v/v N_2 REACTOR FEED.

FIGURE 4. EFFECT OF PRESSURE ON PERFORMANCE OF CATALYST NO. 11 IN HYDROGEN PRODUCTION FROM BEACON CARBON (620°C)